dilution in cold, dry acetone using standardized sodium methoxide in methanol to a bromothymol blue endpoint.

Tosylate Acetolysis Products.—As an example of the usual procedure, 1 ml of the ether stock solution of **3**-OTs or **4**-OTs was added rapidly from a hypodermic syringe to 5 ml of rapidly stirred 0.1 *M* sodium acetate in acetic acid containing about 10 mg of benzene internal standard at room temperature. After reacting at room temperature for about 2 min, the reaction mixture was worked up and the acetolysis products were determined by glpc using a similar procedure to that described earlier[3] for analysis of the acetate and olefin products obtained from acetolysis of *trans*-3-bicyclo[3.1.0]hexyl tosylate.

***endo*- and *exo*-2-Bicyclo[3.1.0]hexyl-3,5-Dinitrobenzoates (3-ODNB and 4-ODNB).**—These were samples, mp 122–124° (lit.[17] mp 124–124.8°) and 96–98° (lit.[17] mp 98–98.6°), respectively, prepared as described elsewhere.[9b]

Stability of *endo*-2-Bicyclo[3.1.0]hexyl Acetate (3-OAc) under Acetolysis Conditions at 100°.—A small sample of **3**-OAc was prepared by the reaction of pure **3**-OH with acetic anhydride in pyridine, bp 103–104° (20 mm), n^{25}D 1.4530 [lit.[19] bp 65–68° (15 mm)]. Two separate Pyrex ampoules were made up, each containing about 0.15 g (1.1 mmol) of **3**-OAc, 0.1 g (0.5 mmol) of 3,5-dinitrobenzoic acid, and 0.1 g (1.2 mmol) of sodium acetate dissolved in 5 ml of dry acetic acid. The ampoules were sealed, heated at 100° for periods of 10 and 54 hr, respectively, and then worked up and analyzed by glpc using the procedure described below for studying the acetolysis products of **3**-ODNB and **4**-ODNB at 100°. The mixtures were found to consist of 82% **3**-OAc, 5% **4**-OAc, and 13% **4**-OAc and 46% **3**-OAc, 23% **4**-OAc, and 31% **5**-OAc, respectively.

3,5-Dinitrobenzoate Acetolysis Products.—As an example of the usual procedure, 0.23 g (0.8 mmol) of **3**-ODNB was dissolved in 8 ml of 0.11 *M* sodium acetate in dry acetic acid, sealed in a Pyrex ampoule, and heated at 100° for 50 hr. The ampoule was then opened, and a cyclohexyl acetate internal standard was weighed in. The contents of the ampoule were poured into 40 ml of *n*-pentane, and the pentane solution was washed with water and 5% aqueous sodium carbonate, dried over magnesium sulfate, and concentrated to about 3 ml by careful distillation through a short glass helices column. Cooling the pentane solution in ice caused **5**-ODNB to crystallize out. This was filtered and weighed, and its structure was determined by comparing its melting point and nmr spectrum with those of an authentic sample[20] prepared by us from **5**-OH. The acetate products were then analyzed by glpc on a 4 m × 0.25 in. column packed half with 20% diethylene glycol succinate (DEGS) and half with 20% diglycerol on 60/80 mesh Chromosorb P. The remaining acetates were then reduced in 50 ml of dry ether with 0.3 g of $LiAlH_4$. After work-up by adding saturated NH_4Cl solution, drying over magnesium sulfate, and concentrating the ether solution to about 4 ml, the resulting alcohols were also analyzed on glpc on the column described above. The reasons for this double analysis procedure and the methods used to identify the volatile products are described elsewhere.[9b] It was found that acetolysis of **3**-ODNB gave 24% **3**-OAc, 28% **4**-OAc, 37% **5**-OAc, 1% **6**-OAc, and 10% **5**-ODNB, and acetolysis of **4**-ODNB gave 23% **3**-OAc, 25% **4**-OAc, 41% **5**-OAc, 1% **6**-OAc, and 10% **5**-ODNB.

Registry No.—**3**-OH, 822-58-2; **3**-OH *p*-nitrobenzoate, 37816-89-0; **3**-OTs, 37816-90-3; **3**-OAc, 698-56-6; **3**-ODNB, 34272-26-9; **4**-OH, 822-59-3; **4**-OH *p*-nitrobenzoate, 37816-94-7; **4**-OTs, 37816-95-8; **4**-ODNB, 34272-27-0.

(19) P. K. Freeman, M. F. Grostic, and F. A. Raymond, *J. Org. Chem.*, **30**, 771 (1965).

(20) L. N. Owen and P. A. Robins, *J. Chem. Soc.*, 320 (1949).

Monocyclic Allenes. The Synthesis of 3,8,9-Cycloundecatriene-1,6-dione and 12-Oxabicyclo[7.2.1]dodeca-5,6,9,11-tetraen-3-one, a Furanophane Containing an Allene Group

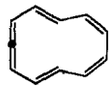
PETER J. GARRATT,* KYRIACOS C. NICOLAOU, AND FRANZ SONDHEIMER

Department of Chemistry, University College, London WC1H OAJ, United Kingdom

Received October 10, 1972

3,8,9-Cycloundecatriene-1,6-dione (**5**) can be prepared from the readily available 4,4,9,9-tetramethoxy-1,6-cyclodecadiene (**2**) *via* the dibromocarbene adduct **3**. The adduct **3** can also be converted into 4,4,10,10-tetramethoxy-6,7-cycloundecadiene-1,2-diol (**8**), which on acid treatment gives 12-oxabicyclo[7.2.1]dodeca-5,6,9,11-tetraen-3-one (**9**), a novel furanophane containing an allene group.

Only a few monocyclic allenes have been prepared in which other functional groups are present. Such molecules are of interest, since the interactions between the functional group and the allene moiety might be unusual. Further, these systems serve as potential precursors of the fully unsaturated monocyclic systems containing an allene group. Heilbronner[1] has suggested that the "Möbius" array of π orbitals in the [4*n*]annulenes might be favored over the "Hückel" array. The introduction of an allene group into a fully conjugated cycle provides an enforced dislocation of the π system. Furthermore, if the allene group is treated as a Möbius array, as suggested by Zimmerman,[2] the possibility exists for a Möbius interaction around the cyclic unsaturated system. The present paper describes the preparation of a number of 11-membered monocyclic allenes containing functional groups, together with a preliminary investigation into methods of converting these molecules into the 12π–11C monocyclic allene **1**.



1

The precursor for the synthesis of the allenes was the bicyclic dibromide **3**. This molecule is obtained[3] by the reaction of dibromocarbene with tetramethoxycyclodecadiene **2**, the latter compound being readily available from naphthalene.[4] Treatment of **3** with methyllithium at −10° gave the allene **4**, mp 75–76°, in 73% yield. The ir spectrum of **4** showed a band at 1980 cm^{-1}, characteristic of an allene,[5] and the nmr

(1) E. Heilbronner, *Tetrahedron Lett.*, 1923 (1964).

(2) H. E. Zimmerman, *Accounts Chem. Res.*, **4**, 272 (1971).

(3) P. J. Garratt, K. C. Nicolaou, and F. Sondheimer, submitted for publication in *J. Amer. Chem. Soc.*

(4) C. A. Grob and P. W. Schiess, *Helv. Chim. Acta*, **43**, 1546 (1960).

(5) L. J. Bellamy, "Infra-Red Spectra of Complex Molecules," 2nd ed, Methuen, London, 1958, p 61.

spectrum was consistent with the assigned structure. Catalytic hydrogenation of **4** in ethyl acetate over palladium on charcoal occurred with concomitant hydrolysis, and cycloundecane-1,6-dione was obtained, identified as its dioxime, mp 229–230°.[6] Hydrolysis of **4** with dilute sulfuric acid in ether yielded 74% of 3,8,9-cycloundecatriene-1,6-dione (**5**), mp 66–67°. The assignment of this structure to **5** was made on the basis of its spectral properties and derivation from **4**. The ir spectrum of **5** had bands at 1960 (allene) and 1705 cm^{-1} (carbonyl), and the nmr spectrum showed signals at τ 4.14–4.44 (m, 2 H, olefin), 4.46–5.00 (m, 2 H, allene) and 6.44–7.36 (8 H, methylene). The electronic spectrum of **5** had maxima at 227 (sh) (ϵ 200) and 294 nm (230) and is similar to that of 3,8-cyclodecadiene-1,6-dione[4,7] and related systems.[3] The long wavelength band presumably arises from a transannular chromophore interaction involving the carbon–carbon double bonds and the carbonyl groups.

Reaction of **5** with tosylhydrazine led to the corresponding bistosylhydrazone, mp 173–174°, in *ca.* 90% yield. Reduction of **5** with lithium aluminum hydride gave the diol **6** as an oil, presumably a mixture of stereomers. Attempts to dehydrate the diol **6** were unsuccessful, either **6** being recovered, or a complex mixture of products being formed. Treatment of **6** with acetic anhydride in pyridine yielded the corresponding diacetate, but pyrolysis of this diacetate led only to dimeric products (mass spectrum).

The dione **14**, formally derived from **5** by the introduction of an additional double bond, appeared to be a suitable precursor of the fully unsaturated allene **1**, and the synthesis of **14** was therefore investigated. Treatment of the dibromide **3** with osmium tetroxide and subsequent hydrolysis of the resulting osmate ester gave the cis diol **7**, mp 81–82°, in 80% yield. The assigned structure **7** was confirmed by the spectral properties, but the relative stereochemistry of the cis hydroxyl groups to the cyclopropyl ring is not known.

Treatment of **7** with a large excess of methyllithium at −10° yielded 70% of the corresponding allene **8**, mp 109–110°. The nmr spectrum of **8** was consistent with the assigned structure and showed the presence of two types of hydroxylic protons (τ 7.00, 7.41), and two types of protons adjacent to hydroxyl (5.60, 6.07). The difference in chemical shift of these sets of protons presumably arises from their relative relationship to the allene group and consequent different magnetic environment.

When **8** was treated with 80% sulfuric acid in ether, 12-oxabicyclo[7.2.1]dodeca-5,6,9,11-tetraen-3-one (**9**), mp 69–70°, was isolated in 63% yield, rather than the anticipated dione **14**. The structure of **9** was confirmed by its chemical and spectral properties. Thus reaction of **9** with 2,4-dinitrophenylhydrazine gave a monohydrazone, mp 202–203°, while catalytic hydrogenation over palladium on charcoal yielded 69% of the bicyclic ketone **10**, mp 38–40°. The ir spectrum of **9** had bands at 1945 (allene) and 1697 cm^{-1} (carbonyl). The nmr spectrum ($CDCl_3$) showed signals at τ 3.90–4.06 (m, 2 H, furan), 4.50–4.70 (m, 1 H, H^7), 5.10–5.43 (m, 1 H, H^5), 6.04–6.88 (m, 5 H, methylene), and 7.07–7.32 (m, 1 H, methylene). The large difference in chemical shift of the allenic protons, H^5, H^7, is presumably due to the shielding of the H^5 proton by the furan ring, similar effects being observed in the metacyclophanes.[8] The high-field methylene proton is attributed to one of the H^4 protons, which is situated in a similar environment to H^5.

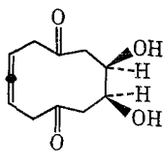
Compound **9** is an interesting substance and appears to be the first bridged aromatic system containing an

(6) D. Devaprabhakara and P. D. Gardner, *J. Amer. Chem. Soc.*, **86**, 648 (1963).

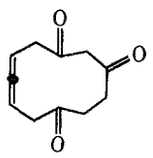
(7) R. C. Cookson and N. S. Warigar, *J. Chem. Soc.*, 2302 (1956); J. Labhart and G. Wagnière, *Helv. Chim. Acta*, **42**, 2219 (1959); K. Kosower, W. D. Closson, H. L. Goering, and J. C. Cross, *J. Amer. Chem. Soc.*, **83**, 2013 (1961); R. C. Cookson and J. Hudec, *J. Chem. Soc.*, 429 (1962).

(8) S. Fujita and T. Mori, *Bull. Chem. Soc. Jap.*, **42**, 1163 (1969); S. Fujita and H. Nozaki, *ibid.*, **44**, 2827 (1971); S. Fuiita, S. Hirano, and H. Nozaki, *Tetrahedron Lett.*, 403 (1972); S. Bradamante, A. Marchesini, and G. Pagani, *ibid.*, 4621 (1971).

allene group. The formation of **9** may occur directly from the ketal **8** or *via* the dione **15**. Protonation on



15



16

the ketal oxygen in **8** or the carbonyl oxygen in **15**, followed by transannular substitution by the remote hydroxyl group, and subsequent dehydration would give **9**. Alternatively dehydration and hydrolysis of **8** may lead to the trione **16**, which would be expected readily to give **9** under acidic conditions.

In a second approach to the dione **14**, the dibromide **3** was oxidized with *m*-chloroperoxybenzoic acid to the epoxide **11**, mp 127–128°, in essentially quantitative yield. The relative stereochemistry of the oxirane and cyclopropane rings is not known, but in view of the findings with related systems,[3] **11** is likely to be the trans stereomer. Treatment of **11** with methyllithium at −10° led to 92% of the allene **12**, mp 122–123°, which on hydrolysis with *p*-toluenesulfonic acid and boron trifluoride etherate in acetone gave the dione **13**, mp 143–144°, in 85% yield. The ir spectrum of **13** showed bands at 1965 (allene) and 1700 cm^{-1} (carbonyl), and the nmr spectrum was consistent with the assigned structure. The electronic spectrum of **13** [λ_{max}^{EtOH} 232 (sh) (ϵ 550), 290 nm (260)] again showed the long wavelength band corresponding to a transannular chromophore interaction characteristic of molecules of this type.[3,4,7]

Attempts to convert **13** into **14** under a variety of conditions were unsuccessful. The only conditions leading to an isolable product were 30% perchloric acid in tetrahydrofuran, which gave the previously isolated furan **9** in 11% yield.

These results indicate that it is difficult to synthesize the dione **14** by a route involving acidic conditions. Other methods for preparing the fully unsaturated allene **1** are now under investigation.

Experimental Section

Melting points were determined on a Kofler hot stage apparatus and are uncorrected. Ir spectra were recorded on either a Unicam SP 200 or a Perkin-Elmer 257 spectrophotometer, and only strong and medium bands are reported. Nmr spectra were recorded on a Varian HA-100 spectrometer as solutions in $CDCl_3$, unless stated otherwise, with TMS as internal standard, and are reported in τ units. Mass spectra were recorded on either an AEI MS 9 or MS 12 spectrometer, and were taken at 70 eV, unless stated otherwise.

Silica for preparative thick layer chromatography (ptlc) was Merck Kieselgel GF_{254}, and that for column chromatography was Hopkins and Williams silica gel (MFC). Bromoform was dried ($CaCl_2$) and freshly distilled over P_2O_5 under N_2. Methyllithium in ether was obtained commercially from Alfa Inorganics. Solvents were May and Baker "R" grade and were purified and dried by standard methods.

11,11-Dibromo-3,3,8,8-tetramethoxybicyclo[8.1.0]undec-5-ene (3).—The diene **2** (12.8 g, 50 mmol)[4] was suspended in pentane (1.5 l.) and potassium *tert*-butoxide (42 g, 373 mmol) was added. The mixture was stirred under N_2 and cooled to 0°; bromoform (63.25 g, 250 mmol) was added slowly over 4 hr. The reaction mixture was allowed to warm to room temperature and was stirred for a further 12 hr. The precipitate was collected and identified as *anti*-6,6,12,12-tetrabromo-3,3,9,9-tetramethoxytricyclo[9.1.0.0^{5,7}]dodecane (19.2 g, 60%).[8] The filtrate was concentrated and chromatographed on silica eluting with ether–pentane, when **11,11-dibromo-3,3,8,8-tetramethoxybicyclo[8.1.0]undec-5-ene (3)** (3.15 g, 18%), mp 134–135° dec (pentane), was obtained: mass spectrum *m/e* 430, 428 (1%), 426, 398, 396 (9%), 394, 367, 365 (15%), 363, 317, 315, 285, 283, 129 (100%), 128, 105, 75; ir (KBr) 2950, 2830, 1435, 1314, 1283, 1195, 1143, 1125, 1075, 1055, 1026, 1015, 950, 915, 835, 762, and 748 cm^{-1}; nmr 4.57 (m, 2 H, olefin) 6.73, 676 (s, 12 H, OCH_3), 7.52–7.70 (m, 4 H, CH_2), 7.98 (m, 2 H), 8.23 (m, 2 H), 8.81 (m, 2 H).

Anal. Calcd for $C_{15}H_{24}O_4Br_2$: C, 42.05; H, 5.60; Br, 37.38. Found: C, 42.37; H, 5.92; Br, 36.98.

Reactions of 3 with Methyllithium. 5,5,10,10-Tetramethoxy-1,2,7-cycloundecatriene (4).—Compound **3** (4.28 g, 10 mmol) was dissolved in dry ether (20 ml), stirred under N_2, and cooled to −80°. Methyllithium (15 ml, 1 M, 15 mmol) was added in one portion; the reaction mixture was allowed to warm to −10° and stirred for 1 hr. Water (15 ml) was then added, the layers were separated, and the aqueous phase was washed with ether (50 ml). The combined organic layers were washed with water (10 ml) and dried ($MgSO_4$), and the solvent was removed by evaporation. The crystalline residue was recrystallized (CH_3OH) to give **5,5,10,10-tetramethoxy-1,2,7-cycloundecatriene (4)** (1.96 g, 73%): mp 75–76°; mass spectrum *m/e* 268 (3%), 253, 236, 221, 205, 204, 173, 147, 141, 109, 101, 88 (100%), 59, 43, 41; ir (KBr) 2960, 2830, 1980, 1458, 1437, 1319, 1268, 1244, 1220, 1192, 1117, 1105, 1078, 1048, 1035, 959, 932, 880, 806, 767, 713, and 622 cm^{-1}; nmr 4.56 (*t*, J = 5 Hz, 2 H, olefin), 4.87–5.14 (m, 2 H, allene), 6.80 (s, 12 H, OCH_3), 7.40–8.04 (m, 8 H, CH_2).

Anal. Calcd for $C_{15}H_{24}O_4$: C, 67.13; H, 9.02. Found: C, 67.00; H, 9.02.

3,8,9-Cycloundecatriene-1,6-dione (5).—Compound **4** (268 mg, 1 mmol) was dissolved in ether (10 ml), sulfuric acid (5%, 4 ml) was added, and the mixture was shaken for 1 hr. The ethereal layer was separated, the aqueous phase was extracted with ether (2 × 20 ml), and the combined ethereal layers were dried ($MgSO_4$). The solvent was removed by evaporation and the crystalline residue recrystallized (ether–pentane) to give **3,8,9-cycloundecatriene-1,6-dione (5)** (130 mg, 74%, prisms): mp 66–67°; mass spectrum *m/e* 176 (2.5%), 158, 148, 94 (100%), 81, 78, 66, 54; ir (KBr) 2980, 1960, 1705, 1339, 1279, 1256, 1220, 1102, 1003, 892, 885, 734, 700, and 673 cm^{-1}; nmr, see discussion; electronic spectrum, see discussion.

Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.97; H, 6.86. Found: C, 74.89; H, 6.94.

Hydrogenation of 4.—Compound **4** (134 mg, 0.5 mmol) was dissolved in ethyl acetate (5 ml); palladium on charcoal (10%, 20 mg) was added and the mixture stirred for 2 hr under an atmosphere of H_2. The catalyst was removed by filtration and the filtrate evaporated. Ptlc of the oily residue, eluting with pentane–ether (1:1) gave **cycloundecane-1,6-dione** (47 mg, 51%):[6] mass spectrum *m/e* 182 (58%), 164, 140, 101, 98, 97, 84, 55; nmr (60 MHz, CCl_4) 7.43–7.90 (m, 8 H, CH_2CO) and 7.90–8.77 (m, 10 H, CH_2).

Treatment of cycloundecane-1,6-dione with $NH_2OH \cdot HCl$ and CH_3CO_2Na gave **cycloundecane-1,6-dioxime**, mp 229–230° (lit.[6] mp 228–229.5, 232–234°).

Reaction of 5 with Tosyl Hydrazide.—Compound **5** (0.53 g, 3 mmol) and tosyl hydrazide (1.12 g, 6 mmol) were dissolved in CH_3OH (20 ml), and concentrated HCl (2 drops) was added. After shaking for 1 hr, the crystalline residue was removed by filtration, washed (CH_3OH), dried, and recrystallized (ethyl acetate) to give **3,8,9-cycloundecatriene-1,6-dione ditosylhydrazone** (1.32 g, 86%): mp 173–174°; mass spectrum *m/e* 328, 278, 246, 173, 156, 139, 92, 91 (100%), 65; ir (KBr) 3220, 3060, 2950, 1628, 1505, 1470, 1430, 1410, 1348, 1332, 1312, 1297, 1188, 1172, 1095, 1040, 1030, 930, 898, 878, 825, 720, 710, and 680 cm^{-1}.

Reduction of 5 with Lithium Aluminum Hydride. 3,8,9-Cycloundecatriene-1,6-diol (6).—$LiAlH_4$ (38 mg, 1 mmol) was suspended in ether (10 ml) and stirred under N_2; a solution of the dione **5** (150 mg, 0.85 mmol) in ether (5 ml) was added dropwise over 20 min. After stirring for an additional 2 hr the mixture was neutralized with dilute HCl, the organic layer separated, and the aqueous phase extracted with ether (2 × 20 ml). The combined ethereal layers were washed with water (3 ml) and dried ($MgSO_4$); the solvent was removed by evapora-

tion. The oily residue was chromatographed on silica eluting with ether to give **3,8,9-cycloundecatriene-1,6-diol (6)** (130 mg, 85%) as a colorless oil: mass spectrum M^+ 180.1144, $C_{11}H_{16}O_2$ requires M^+ 180.1150, *m/e* 180 (0.7%), 162, 144, 129, 118, 105, 91, 79, 55, 53, 41 (100%); ir ($CHCl_3$) 3450, 3010, 2930, 1970, 1453, 1395, 1243, 1045, 957, 898, and 880 cm^{-1}; nmr 4.38–4.71 (m, 2 H, olefin), 4.73–5.17 (m, 2 H, allene), 5.78–6.42 (m, 2 H, CHOH), 7.46–7.92 (m, 8 H, CH_2), and 8.28 (s, 2 H, OH).

3,8,9-Cycloundecatriene-1,6-diol Diacetate.—The diol **6** (90 mg, 0.5 mmol) was added to a mixture of acetic anhydride (1 ml) and pyridine (1 ml) and the mixture heated to reflux for 30 min. After cooling, the mixture was poured into hydrochloric acid (1 *N*, 20 ml) and extracted with ether (2 × 50 ml). The ethereal extract was washed with water (5 ml) and dried (K_2CO_3); the solvent was removed by evaporation. Chromatography of the residue on silica gave **3,8,9-cycloundecatriene-1,6-diol diacetate** (115 mg, 87%) as a colorless oil: mass spectrum M^+ 264.1369, M^+ requires 264.1362, *m/e* 144, 143, 129, 117, 92, 79, 67, 66, 55, 43 (100%); at 20 eV 264, 204, 162 also observed; ir 3000, 2950, 1970, 1735, 1450, 1440, 1385, 1245, 1028, 960, 885, 855, 735, and 715 cm^{-1}; nmr (CCl_4) 4.36–4.73 (m, 2 H, olefin), 4.84–5.13 (m, 2 H, allene), 5.0–5.5 (m, 2 H, $CHOCOCH_3$), 7.12–7.92 (m, 8 H, CH_2), and 8.05 (s, 6 H, $OCOCH_3$).

Reaction of 3 with Osmium Tetroxide. 11,11-Dibromo-3,3,8,8-bicyclo[8.1.0]undecane-5,6-diol (7).—Compound **3** (2.14 g, 5 mmol) was dissolved in pyridine (50 ml), and a solution of osmium tetroxide (1.27 g, 5 mmol) in benzene (25 ml) was added. The reaction mixture was stirred for 2 hr, diluted with pentane (750 ml), and filtered. The precipitate of osmate ester (4.2 g) was suspended in ethanol (100 ml), and a solution $Na_2SO_4 \cdot 7H_2O$ (12.6 g, 50 mmol) in water (50 ml) was added. The mixture was heated to reflux for 1 hr, cooled, and filtered. $CHCl_3$ (250 ml) and water (100 ml) were added to the filtrate; the organic layer was separated, washed with water (10 ml), and dried ($MgSO_4$). The solvent was removed by evaporation and the crystalline residue recrystallized ($CHCl_3$–ether) to give **11,11-dibromo-3,3,8,8-tetramethoxybicyclo[8.1.0]undecane-5,6-diol** (7) (2.15 g, 80%): mp 81–82; mass spectrum *m/e* 367, 365 (5%), 363, 337, 335 (3%), 333, 300, 298, 287, 285, 268, 266, 254, 252, 177, 174, 146, 145, 132, 128, 108, 96, 95, 94 (100%); ir (KBr) 3450, 2955, 1465, 1415, 1308, 1287, 1207, 1160, 1145, 1125, 1055, 1036, 1016, 975, 832, 725, and 685 cm^{-1}; nmr 6.10–6.29 (m, 2 H, CHOH), 6.76 (s, 6 H, OCH_3), 6.78 (s, 6 H, OCH_3), 7.19 (s, 2 H, OH), 7.60–8.38 (m, 8 H, CH_2), and 8.60–8.90 (m, 2 H, cyclopropane).

Anal. Calcd for $C_{15}H_{26}O_6Br_2$: C, 38.98; H, 5.67; Br, 34.58. Found: C, 38.74; H, 5.67; Br, 34.24.

Reaction of 7 with Methyllithium. 4,4,10,10-Tetramethoxy-6,7-cycloundecadiene-1,2-diol (8).—Compound **7** (462 mg, 1 mmol) was suspended in dry ether (40 ml) under N_2, stirred, and cooled to −80°. Methyllithium (6 ml, 1 *M*, 6 mmol) was added in one portion; the mixture was allowed to warm to −10° and was stirred for 30 min. Water (5 ml) was added and the mixture separated. The ethereal layer was washed with water (5 ml) and dried ($MgSO_4$) and the solvent removed by evaporation. The crystalline residue was recrystallized (ether–pentane) to give **4,4,10,10-tetramethoxy-6,7-cycloundecadiene-1,2-diol (8)** (210 mg, 70%): mp 109–110°; mass spectrum *m/e* 270, 239, 224, 220, 207, 206, 189, 174, 170, 147 (100%), 146, 118, 117, 109, 94, 57; ir (KBr) 3450, 2950, 2930, 1965, 1460, 1440, 1355, 1335, 1320, 1300, 1260, 1227, 1200, 1128, 1069, 1044, 988, 900, 880, 836, 815, 840, and 685 cm^{-1}; nmr 4.75–5.16 (m, 2 H, allene), 5.48–5.72 (m, 1 H, CHOH), 5.97–6.16 (m, 1 H, CHOH), 6.78 (s, 6 H, OCH_3), 6.82 (s, 6 H, OCH_3), 7.00 (s, 1 H, OH), 7.41 (s, 1 H, OH), and 7.46–8.26 (m, 8 H, CH_2).

Anal. Calcd for $C_{15}H_{26}O_6$: C, 59.58; H, 8.67. Found: C, 59.17; H, 8.49.

12-Oxabicyclo[7.2.1]dodeca-5,6,9,11-tetraen-3-one (9).—Compound **8** (151 mg, 0.5 mmol) was dissolved in ether (50 ml), and sulfuric acid (80%, 2 ml) added. The mixture was shaken for 5 min; the ethereal layer was separated, washed with water (3 × 2 ml), and dried ($MgSO_4$). The solvent was removed by a stream of N_2, and the crystalline residue was recrystallized (pentane) to give **12-oxabicyclo[7.2.1]dodeca-5,6,9,11-tetraen-3-one (9)** (55 mg, 63%): mp 69–70°; mass spectrum M^+ 174.0677, $C_{11}H_{10}O_2$ requires M^+ 174.0681, *m/e* 174 (36%), 146, 94 (100%); ir (KBr) 2920, 1945, 1697, 1665, 1605, 1558, 1436, 1405, 1310, 1260, 1237, 1222, 1213, 1158, 1150, 1020, 1009, 988, 970, 940, 928, 903, 875, 858, 840, 783, and 710 cm^{-1}; nmr, see discussion; λ_{max}^{EtOH} 227 nm (ε 3000), 251 (1500), 310 (230), 318 (260), and 330 (180).

Anal. Calcd for $C_{11}H_{10}O_2$: C, 75.84; H, 5.79. Found: C, 75.91; H, 5.93.

Hydrolysis of the epoxide **13** (96 mg, 0.5 mol) in THF (10 ml) with perchloric acid (30%, 5 ml) at room temperature for 3 hr also gave **9** (11%), identical in all observed respects with that obtained from the diol.

Treatment of **9** with 2,4-dinitrophenylhydrazide and concentrated HCl in glyme at 70° gave the corresponding **2,4-dinitrophenylhydrazone,** (76%), mp 202–203°, pale orange crystals, mass spectrum *m/e* 354 (54%).

Anal. Calcd for $C_{17}H_{14}N_4O_5$: C, 57.62; H, 3.98; N, 15.81. Found: C, 57.19; H, 4.23; N, 15.48.

Hydrogenation of 9.—Compound **9** (34.8 mg, 0.2 mol) was dissolved in ethyl acetate (5 ml), palladium on charcoal (10%, 10 mg) was added, and the mixture was stirred under an atmosphere of hydrogen for 30 min. The catalyst was removed by filtration, and the filtrate was evaporated to give an oily residue. Ptlc on silica with pentane–ether (1:1) gave **12-oxabicyclo[7.2.1]-dodecan-3-one (10)**, (24 mg: 69%): mp 38–40°; mass spectrum M^+ 182.1299, $C_{11}H_{18}O_2$ requires M^+ 182.1307, *m/e* 182 (25%), 180, 164, 153, 139, 125, 113, 98, 82, 80, 69, 55, 41 (100%); ir (CCl_4) 2930, 2860, 1702, 1473, 1450, 1365, 1354, 1275, 1200, 1140, 1090, 1065, and 1040 cm^{-1}; nmr 5.58–5.84 (m, 1 H), 5.88–6.20 (m, 1 H), 7.70–7.50 (m, 2 H), and 7.60–8.92 (m, 14 H).

Treatment of **10** with hydroxylamine hydrochloride and CH_3CO_2Na in CH_3OH–H_2O gave the oxime (82%): mp 123–124°; mass spectrum M^+ 197.1424, $C_{11}H_{19}NO_2$ requires M^+ 197.1416, *m/e* 197 (25%).

Reaction of 3 with *m*-Chloroperoxybenzoic Acid. 12,12-Dibromo-3,3,9,9-tetramethoxy-6-oxatricyclo[9.1.0.0^{5,7}]dodecane (11).—Compound **3** (2.14 g, 5 mmol) was dissolved in chloroform (50 ml) and *m*-chloroperoxybenzoic acid (12.0 g, 80%, 5.5 mmol) was added. The solution was stirred for 15 hr, excess of a saturated solution of sodium sulfite was added, and the mixture was neutralized with aqueous potassium hydroxide. The organic layer was separated, washed with water (2 × 5 ml), and dried ($MgSO_4$); the solvent was removed by evaporation. The crystalline residue was recrystallized ($CHCl_3$–pentane) to give **12,12-dibromo-3,3,9,9-tetramethoxy-6-oxatricyclo[9.1.0.0^{5,7}]-dodecane** (11) (2.0 g, 90%): mp 127–128°; mass spectrum *m/e* 382, 380 (22%), 378, 364, 362, 333, 331, 301, 299, 237, 221, 219, 129, 101 (100%), 89, 88; ir (KBr) 2960, 2840, 1465, 1455, 1315, 1275, 1162, 1140, 1120, 1077, 1050, 1012, 975, 962, 840, 818, 780, and 727 cm^{-1}; nmr 6.74 (s, 12 H, OCH_3), 7.04 (d, *J* = 10 Hz, 2 H, epoxide), 7.57–7.97 (m, 4 H, CH_2), 8.17–8.62 (m, 4 H, CH_2), and 8.80 (ddd, *J* = 2, 7, 13 Hz, 2 H, cyclopropane).

Anal. Calcd for $C_{15}H_{24}O_5Br_2$: C, 40.56; H, 5.45; Br, 35.98. Found: C, 40.34; H, 5.30; Br, 35.90.

Reaction of 11 with Methyllithium. 3,3 9,9-Tetramethoxy-12-oxabicyclo[9.1.0]dodeca-5,6-diene (12).—Compound **11** (888 mg, 2 mmol) was suspended in ether (50 ml), stirred under N_2, and cooled to −80°. Methyllithium (3 ml, 1 *M*, 3 mmol) was added in one portion, and the reaction mixture was allowed to warm to −10° and stirred for 30 min. Water (5 ml) was added; the organic layer was separated, washed with water (2 × 3 ml), and dried ($MgSO_4$). The solvent was removed by evaporation and the crystalline residue recrystallized (ether–pentane) to give **3,3,9,9-tetramethoxy-12-oxabicyclo[9.1.0]dodeca-5,6-diene (12)** (525 mg, 92%): mp 122–123°; mass spectrum *m/e* 284 (2%), 269, 253, 252, 237, 221 ,185, 161 148, 136, 129, 117, 101, 88 (100%), 59, 58, 57, 55, 43; ir (KBr) 2950, 2830, 1965, 1475, 1445, 1420, 1395, 1350, 1342, 1315, 1285, 1254, 1241, 1200, 1190, 1162, 1142, 1125, 1105, 1082, 1060, 1040, 1018, 995, 970, 948, 912, 904, 835, 825, 795, 782, 767, and 715 cm^{-1}; nmr 4.92 (m, 2 H, allene), 6.76, 6.78, 6.81 (s, 12 H, OCH_3), 6.84–7.12 (m, 2 H, epoxide) and 7.24–8.60 (m, 8 H, CH_2).

Anal. Calcd for $C_{15}H_{24}O_5$: C, 63.36; H, 8.51. Found: C, 63.32; H, 8.50.

12-Oxabicyclo[9.1.0]dodeca-5,6-diene-3.9-dione (13).—Compound **12** (142 mg, 0.5 mmol) was dissolved in acetone (25 ml), and a solution of *p*-toluenesulfonic acid (10 mg) in water and boron trifluoride etherate (1 drop) were added. The mixture was shaken for 10 min, the solvent was removed by evaporation, and water (1 ml) added; a precipitate formed. Ether (200 ml) was added and the mixture was shaken. The ethereal layer was

separated, washed with water (20 ml), and dried ($MgSO_4$). Evaporation of the solvent gave a crystalline residue which was recrystallized (ether–pentane) to give **12-oxabicyclo[9.1.0]-dodeca-5,6-diene-3,9-dione (13)** (82 mg, 85%): mp 143–144°; mass spectrum (15 eV) *m/e* 192 (2.5%), 174, 164, 150, 120, 110, 108, 107 (100%), 94, 66, 65, 55; ir (KBr) 2980, 2930, 2880, 1965, 1700, 1467, 1438, 1418, 1390, 1340, 1300, 1270, 1249, 1200, 1112, 1090, 1027, 986, 968, 931, 886, 842, 793, and 714 cm^{-1}; nmr 4.44–4.80 (m, 2 H, allene), 6.40–6.64 (m, 2 H, epoxide), and 6.69–7.56 (m, 8 H, CH_2); electronic spectrum, see discussion.

Anal. Calcd for $C_{11}H_{12}O_3$: C, 68.73; H, 6.29. Found: C, 68.42; H, 6.38.

Registry No.—**2**, 37709-72-1; **3**, 37709-73-2; **4**, 37780-37-3; **5**, 37709-74-3; **5** ditosylhydrazone, 37709-75-4; **6**, 37709-76-5; **6** diacetate, 37709-77-6; **7**, 37709-78-7; **8**, 37709-79-8; **9**, 37709-80-1; **9** dinitrophenylhydrazone, 37709-81-2; **10**, 37709-82-3; **10** oxime, 37709-83-4; **11**, 37709-84-5; **12**, 37709-85-6; **13**, 37709-86-7.

Acknowledgment.—We thank the Science Research Council, U. K., for a studentship to K. C. N.

Addition Reactions of *cis,trans*-1,5-Cyclodecadiene[1]

JAMES G. TRAYNHAM* AND HSIN HSIONG HSIEH[2]

Coates Chemical Laboratories, Louisiana State University, Baton Rouge, Baton Rouge, Louisiana 70803

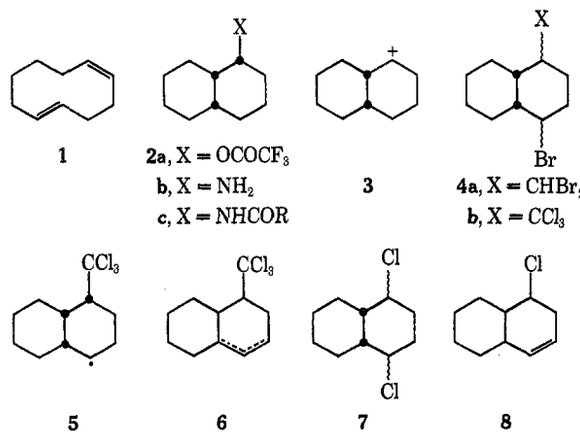
Received July 25, 1972

A variety of cationic, radical, and methylene reagents add selectively to *cis,trans*-1,5-cyclodecadiene. Noncyclic reagents (multistep addends), whether cationic or radical, lead to substituted *cis*-decalins, while methylene reagents give cyclopropane derivatives (preferred attack on trans C=C). The stereochemistry of the products has been established by nmr techniques and delineates to a substantial degree such mechanistic details of the addition process as position of initial attack and degree of concertedness. The stereoselectivity in product formation is usually higher with the cationic than with the radical reagents, and, in several reactions, it is sufficiently high to be useful in synthesis.

A few years ago, a report from our laboratory demonstrated the potential of *cis,trans*-1,5-cyclodecadiene (**1**) for differentiating between single-step and multistep attack of addends on the two carbons of an olefinic linkage.[3] Subsequently, several short communications showed much the same potential in the relative rates of exo addition to norbornene and to 7,7-dimethylnorbornene.[4] Both studies led to the conclusion, among others, that oxymercuration proceeds in steps rather than by a cyclic mechanism, even though cis additions are reported.

Our original investigation was limited to several reagents which add by a cyclic or single-step mechanism and to several ionic reagents. We have now extended the investigation to include radical addends as well as other ionic and methylene reagents. Additions to **1** by noncyclic reagents, whether cationic or radical, lead to substituted *cis*-decalins, usually with a substantial degree of stereoselectivity that can be useful in syntheses. This paper reports, we believe, the first examples of cycloadditions of radical reagents with the C_{10} ring system. Methylenes and other reagents which add to both carbons in the olefinic linkage without forming a trivalent carbon intermediate give 5,6-disubstituted cyclodecenes, with preference for addition to the trans rather than the cis C=C.[3] Frequently the two courses of addition can be differentiated easily by monitoring the C=CH nmr absorptions by an equimolar mixture of the diene **1** and the addend. The various addends are discussed in groups according to potential synthetic usefulness as well as to mechanism.

We have previously reported the photoisomerization of **1** to *cis,cis*-1,5-cyclodecadiene and the relative reactivities of the isomeric dienes toward trifluoroacetic acid and with respect to thermal isomerization to *cis*-1,2-divinylcyclohexane (**1** reacts faster than its isomer in both cases).[5]



Ionic Reagents. Trifluoroacetic Acid.—When a sample of diene **1** is added to trifluoroacetic acid, a spontaneous, exothermic reaction produces *cis*-1-*cis*-decalyl trifluoroacetate (**2a**) in nearly quantitative yield. Saponification of the ester yields *cis*-1-*cis*-decalol, an alcohol for which several preparations have been described. We believe this preparation to be the easiest

(1) (a) Based upon the Ph.D. dissertation of H. H. H., Louisiana State University, Baton Rouge, Aug 1970. (b) The maior portion of this manuscript was prepared while J. G. T. was a NATO Senior Fellow in Science at the Institut für organische Chemie, Universität des Saarlandes, Saarbrücken, Germany; J. G. T. acknowledges with appreciation the courtesies extended to him by Professor M. Hanack and other members of the institute. (c) Supported in part by a grant from the National Science Foundation (NSF GP 8228).

(2) (a) Acknowlegment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for an American Chemical Society–Petroleum Research Fund Final Year Graduate Fellowship, 1969–1970, to H. H. H. (b) The financial assistance from the Charles E. Coates Memorial Fund, donated by George H. Coates, for preparation of the Ph.D. dissertation of H. H. H. is gratefully acknowledged.

(3) J. G. Traynham, G. R. Franzen, G. A. Knesel, and D. J. Northington, Jr., *J. Org. Chem.*, **32**, 3285 (1967).

(4) H. C. Brown and K.-T. Liu, *J. Amer. Chem. Soc.*, **92**, 200, 3502 (1970); H. C. Brown and J. H. Kawakami, *ibid.*, **92**, 201 (1970); H. C. Brown and K.-T. Liu, *ibid.*, **93**, 7335 (1971).

(5) J. G. Traynham and H. H. Hsieh, *Tetrahedron Lett.*, 3905 (1969).